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### Hydrogenation of edible oils and fats

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## 6. Conclusions



*The chapters of this thesis report on various parts of an investigation of the nickel-catalyzed hydrogenation of edible oils, starting from the intrinsic reaction kinetics of the monounsaturated FAME hydrogenation. The rate equations obtained could be applied successfully in the extension to diene kinetics and in the measurement of intraparticle diffusion coefficients ( $D_e$ ) from hydrogenation experiments. Apart from this, independent experiments were performed for  $D_e$  and adsorption coefficients ( $K_s$ ). This chapter is a brief general discussion on the methods applied and on the results.*

## 6.1. Methodology

In this section, the methodology of the research is discussed, per chapter:

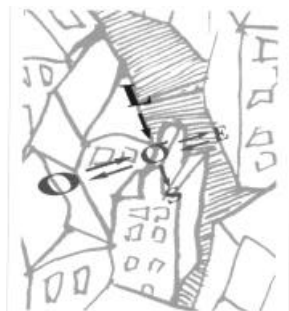


**Monoene Kinetics.** Kinetic expressions for the hydrogenation reaction rates of methyl oleate and elaidate were derived on the basis of the Horiuti–Polanyi mechanism, in which the half-hydrogenated surface intermediate is the key component. Kinetic experiments in the absence of diffusion limitation were carried out for  $333 \leq T \leq 443$  K,  $0.02 \leq P_{H_2} \leq 0.50$  MPa, and various compositions of oleate, elaidate and stearate, in constant and variable-hydrogen pressure experiments.

The experiments were fitted in both the conversion and the time domain, and the rate equations derived were statistically evaluated on the ability of describing the experimental series. For this purpose, Bartlett's test was used. The reaction scheme was constructed from adsorption of the reactants, followed by the formation of the half-hydrogenated intermediate (first hydrogen insertion) and the second hydrogen insertion to the fully saturated molecule. From this scheme, we derived sets of rate equations, based on all possible rate limiting steps.

The model with a rate limitation in the first hydrogen insertion in the double bonds of adsorbed oleate (*cis*) and elaidate (*trans*) proved to be the most likely, rather than adsorption steps or the irreversible second hydrogen insertion step to the fully saturated stearate. In this way, we have used a relatively simple system to derive and test a systematical approach in determining the key reaction steps of an otherwise complex system, which enables a further straightforward modeling of other kinetic steps or mass transfer limitations.

The selected rate equations also showed that the isomerization constant preferably must be obtained from independent isomerization experiments rather than from fitting hydrogenation data in kinetic models, because of the effect of inaccuracies in the hydrogenation rate constants on the isomerization constant.



**Diene kinetics.** The kinetic rate expressions for the hydrogenation of double unsaturated fatty acid methyl esters (FAME) were based on an extension of the model for hydrogenation of monounsaturated FAMEs of chapter 2. The experimental series contained both constant and variable hydrogen pressure experiments. The parameters were obtained by a stepwise evaluation of the rate equations on the

experimental results.

Assuming similar rate determining steps in the diene hydrogenation, and similar adsorption constants for the *cis* and *trans* isomers of diene, the monoene model could be relatively easily extended to dienes. Using apparent kinetics or power law kinetics, this extension would have needed the introduction of a number of unknown kinetic parameters (for all *cis* and *trans* isomers of dienes), which are difficult to determine experimentally. With the addition of the preferential adsorption of dienes relative to monoenes only, the developed rate equations appear to be capable of describing accurately both the observed diene selectivity and the monoene *cis-trans* isomers transients in diene hydrogenations at the conditions tested ( $324 \leq T \leq 363$  K and  $0.3 \leq P_{H_2} \leq 3.5$  MPa).

Due to the larger experimental pressure range applied in the diene hydrogenation experiments, relative to the monoene experiments, it was necessary to determine the hydrogen adsorption parameters separately from the kinetic constants.



**Intraparticle Diffusion.** The intrinsic rate equations for monoene hydrogenation were used to derive intraparticle diffusion coefficients under reaction conditions. FAME hydrogenations in Pricat 9910 (sample 1992) at  $T = 443$  K, appear to be controlled by intraparticle diffusion of hydrogen. As far as we know, this is the first result on intraparticle hydrogen diffusion in FAME hydrogenation on supported nickel catalysts. In edible oil (triacylglyceride, TAG) hydrogenation, both at 373 K and 443 K, TAG appears to be diffusion limited rather than  $H_2$ , which is in line with literature. For the diffusion limited conditions, we were able to determine the relevant intraparticle effective diffusion coefficients for both hydrogen and TAG.

Under inert conditions, intraparticle pore diffusion was measured for paraffins, triacylglycerides and methyl esters of fatty acids in Pricat 9933 by a so-called HPLC tracer technique. Because of the small particles and the relatively fast intraparticle mass transfer, these experiments are unique in the literature. The response peaks indicate a uniform packing of the particles over the column and an absence of by-passes in the column packing. Intraparticle diffusivities of methyl palmitate, *n*-hexadecane, trioleate, and soybean oil in MCT oil could be measured.



**Adsorption.** For studying adsorption phenomena of saturated and unsaturated fatty acid methyl esters, a novel type of mixing cell was developed, which could mix slurries with solids loads as high as 60 w/w%. Also experiments were carried out with tracer pulse experiments.

In chromatographic experiments with *n*-octane as an eluent, methyl palmitate adsorbed on the deactivated nickel-silica surface, while adsorption of *n*-hexadecane was absent, which shows the interaction of the methyl ester group with the silica surface. With medium chain triglyceride oil as an eluent, the adsorption phenomena of methyl palmitate and trioleate disappeared.

To investigate double bond adsorption at reaction conditions, activated Raney nickel catalyst was used in batch adsorption experiments. The batch adsorption experiments showed that monounsaturated FAMES absorb preferentially relative to saturated FAMES. Also chain shortening of C18 to C17 and further (demethylation), was observed as well as the formation of conjugated species of the conjugatable double unsaturated methyl linoleate. Both effects could be used to prove qualitatively that methyl linoleate preferentially adsorbs relative to monounsaturated FAMES on the nickel surface.

## 6.2. Results

A systematical evaluation of all kinetic and transport processes of monoene and diene hydrogenation and isomerization on supported nickel catalysts has led to the following insights in the hydrogenation of edible oils and their fatty acid methyl esters. As discussed in the different chapters, our findings are in line with the elaborate literature on results as far as available.

In hydrogenation of a mixture of methyl oleate (O) and methyl elaidate (E), the hydrogenation and isomerization process is not limited by intraparticle diffusion in the range  $333 \leq T \leq 428$  K and  $0.02 \leq P_{H_2} \leq 0.50$  MPa (Pricat 9910, sample 1992,  $d_p = 8.4$  mm). At these conditions, the intrinsic kinetics of the hydrogenation process can be described by Langmuir kinetics with competitive adsorption between the monounsaturated compounds ( $K_M$ ), O and E, versus saturated ( $K_S$ ), S ( $K_M/K_S=3.3$ , independent of temperature). The selected rate equations (see e.g., eqs 1 and 2 of the abstract) predict O and E being directly irreversibly hydrogenated to stearate, at almost an equal conversion rate. Besides, O is favorably isomerized to E, which was detected

as a reversible reaction. Activation energies of 30 kJ/mol for the hydrogenation reactions of oleate and elaidate and 44 kJ/mol for the isomerization reaction were found. The conversion rates of O and E, both hydrogenation and isomerization, appeared to depend on the hydrogen pressure, which implies that at the conditions tested, the formation of *trans* during the reaction is not a function of the hydrogen pressure.

Modeling of intraparticle diffusion limitation, applying the rate equations of the monoene kinetics, showed that *trans* formation during the reaction is influenced by FAME or TAG intraparticle diffusion limitation, rather than of hydrogen. Therefore, in FAME hydrogenation, any hydrogen diffusion limitation only decreases the overall conversion rates of O and E, without disturbing the ratio of O and E. At  $T = 443$  K and  $0.02 \leq P_{H_2} \leq 0.50$  MPa, a decrease of the catalyst efficiency of 0.25 is found from which  $D_{e,H_2} = (1.6 \pm 0.7) \times 10^{-10}$  m<sup>2</sup>/s could be calculated for Pricat 9910 (sample 1992).

Intraparticle mass transfer of the TAG molecules appears to be limited by diffusion at lower temperatures compared to the much smaller FAME molecules, which also ruled out possible hydrogen diffusion limitation. From a series of TAG experiments at similar conditions as the FAME experiments,  $D_{e,TAG} = (4.5 \pm 2.2) \times 10^{-13}$  m<sup>2</sup>/s at  $T = 373$  K to  $D_{e,TAG} = (3.3 \pm 1.1) \times 10^{-12}$  m<sup>2</sup>/s at  $T = 443$  K were determined for Pricat 9910.

$D_{e,TAG}$  was also obtained from independent HPLC experiments with a similar catalyst (Pricat 9933, sample 1992):  $4 \times 10^{-12} \leq D_{e,TAG} \leq 7 \times 10^{-12}$  m<sup>2</sup>/s ( $T = 313$  K). Corrected for temperature, the relatively large value of  $D_e$  in HPLC experiments indicate a small hindrance in the pores, which can be ascribed to a large influence of intercrystalline holes, relative to the crystalline pores. The observed  $D_{e,TAG}$  under reaction conditions appeared to be 10-fold lower than measured with a tracer technique under nonreaction conditions. This difference could be qualitatively explained from the fact that tracer techniques merely measure the diffusivity in the macropores, whereas the chemical reaction mostly occurs in micropores.

The extension of the monoene model to dienes for Pricat 9910 enabled the determination of the preferential adsorption of diene to monoene. The fitted value of the added adsorption parameter  $\tilde{K}_D$  results in diene adsorption constants of  $9.2 \leq \tilde{K}_D \leq 18.3$  at  $323 \leq T \leq 393$  K. Since  $\tilde{K}_D$  denotes the ratio of diene over saturated adsorption, these values show that preferent adsorption of the double bonds relative to the

adsorption of saturated FAME increases with temperature and, because  $K_M/K_S$  is constant, so does the preferential adsorption of diene over monoene.

The adsorption experiments confirm, qualitatively, the preferential adsorption of diene over monoene, but also showed the strong interaction of the methyl esters with the silica support. The HPLC experiments delivered the linear adsorption enthalpy  $\Delta H(K_s) = -42 \pm 5$  kJ/mol ( $313 \leq T \leq 353$  K) for adsorption of methyl palmitate, compared to the absence of adsorption of *n*-hexadecane. On pure nickel and under reaction conditions, the double bonds strongly adsorb at nickel, with a selectivity coefficient of  $\Omega > 100$  of monoene, relative to saturated FAME. However, on silica-supported-nickel, maybe due to the methyl ester-support interaction, the difference between monoene and saturated FAME is highly reduced to about ( $K_M/K_S=3$ ).

These results enables further steps in the labyrinth of the catalyst particle and reaction mechanism and form a basis for a more thorough investigation of the complex reaction network of the nickel-catalyzed edible oil hydrogenation.